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## (54) HOT-DIP Sn-Mg COATED STEEL SHEET

## (57)Abstract:

PROBLEM TO BE SOLVED: To provide Pb-free hot-dip Sn-Mg coated steel sheet having excellent corrosion resistance and suitably used for automobile fuel tank material in particular.

SOLUTION: The hot-dip Sn-Mg coated steel sheet has a plating structure containing 0.1-4% Mg and having  $\leq 20.0$  mm major axis of crystal of plating metal at the outermost surface.

Further, there are cases such that: 0.5-20% Zn and 0.01-2% Ca are contained in the plating layer; Ni, Co and Cu are contained in an alloy layer; and an aftertreatment layer consisting of an inorganic compound, an organic compound or a combination of the both is present at the outermost surface layer. Accordingly, the plated steel sheet has characteristics suitable for a fuel tank material free from Pb.

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ABSTRACT:

**PROBLEM TO BE SOLVED:** To provide Pb-free hot-dip Sn-Mg coated steel sheet having excellent corrosion resistance and suitably used for automobile fuel tank material in particular.

**SOLUTION:** The hot-dip Sn-Mg coated steel sheet has a plating structure containing 0.1-4% Mg and having  $\leq 20.0$  mm major axis of crystal of plating metal at the outermost surface. Further, there are cases such that: 0.5-20% Zn and 0.01-2% Ca are contained in the plating layer; Ni, Co and Cu are contained in an alloy layer; and an aftertreatment layer consisting of an inorganic compound, an organic compound or a combination of the both is present at the outermost surface layer. Accordingly, the plated steel sheet has characteristics suitable for a fuel tank material free from Pb.

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**CLAIMS**

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[Claim(s)]

[Claim 1] The melting Sn-Mg system plating steel plate characterized by having an alloy layer with a thickness of 3.0 micrometers or less on a steel plate front face, and for a presentation containing Mg 0.1 to 4% by mass % on the front face, and for the remainder serving as Sn from an unescapable impurity, and the major-axis dimension of the plating metallic crystal in the maximum front face having a plating layer 20mm or less.

[Claim 2] The melting Sn-Mg system plating steel plate according to claim 1 characterized by having a melting Sn-Mg plating layer on a steel plate front face, and the presentation of a plating layer containing 74 - 99.9% of Sn by mass %.

[Claim 3] The melting Sn-Mg system plating steel plate according to claim 1 or 2 characterized by the presentation of a plating layer containing one sort of 0.5 - 20% of Zn, and 0.01 - 2% of calcium, or two sorts or more by weight % in addition to Sn and Mg.

[Claim 4] claims 1-3 characterized by having an alloy layer with a thickness of 3.0 micrometers or less which contains one sort of nickel, Co, and Cu, or two sorts or more 0.5% or more in total on a steel plate front face, for a presentation containing Mg 0.1 to 4% by mass % on the front face, and for the remainder serving as Sn from an unescapable impurity, and the major-axis dimension of the plating metallic crystal in the maximum front face having a plating layer 20mm or less -- a melting Sn-Mg system plating steel plate given in either.

[Claim 5] claims 1-4 characterized by having the after-treatment layer which becomes a plating layer front face from an inorganic compound, an organic compound, or its composite -- a melting Sn-Mg system plating steel plate given in either.

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[Translation done.]

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention has the outstanding corrosion resistance and junction nature, and workability, and relates to a motor fuel tank ingredient, a home electric machine, and a melting Sn-Mg system plating steel plate suitable as an industrial machine ingredient.

[0002]

[Description of the Prior Art] Conventionally, as a fuel tank ingredient, the outstanding Pb-Sn alloy-plating steel plates, such as corrosion resistance, workability, and solder nature (weldability), are mainly used, and it is broadly used as an automotive fuel tank until now. On the other hand, the Sn-Zn alloy-plating steel plate has mainly been manufactured with electroplating electrolyzed in the water solution containing Zn and Sn ion, as indicated by JP,52-130438,A. The Sn-Zn alloy-plating steel plate which makes Sn a subject is excellent in corrosion resistance or solder nature, and that to electronic parts etc. are used. [ many ] On the other hand, the knowledge of having the property this Sn-Zn plating steel plate excelled [ property ] in the motor fuel tank application is carried out, and the melting Sn-Zn plating steel plate which controlled the plating organization is indicated in JP,8-269733,A, JP,8-269734,A, etc.

[0003]

[Problem(s) to be Solved by the Invention] The Pb-Sn alloy-plating steel plate used as an automotive fuel tank material is shifting towards the formation of Pb free along with a rise of earth environment recognition in recent years, although the properties (for example, workability, tank inside corrosion resistance, solder nature, seam welding nature, etc.) which were excellent in various kinds have been accepted and used regularly. On the other hand, the Sn-Zn electrical-and-electric-equipment alloy-plating steel plate has been used for the application which is mainly demanded [ nature / solder ] and which is not so severe as electronic parts.

[0004] The above mentioned melting Sn-Zn plating steel plate has the corrosion resistance which surely was excellent, workability, and solder nature. However, the further corrosion resistance improvement is called for and sacrifice corrosion prevention ability is not fully demonstrated in recent years at the edge at which, as for the sacrifice corrosion prevention effectiveness of the narrow cut section (crack which is attained to a ferrite) of width, neither the case where the width of the cut section of a certain thing is large to some extent, nor plating is covered with the Sn-Zn plating steel plate.

[0005] Especially in the salt spray test supposing a salt damage environment, a period until it results in rust generating is short, and cannot say that it is enough. If the amount of Zn becomes high too much, the subject of a plating layer shifts to Zn from Sn, and although what is necessary is just to increase the addition of Zn in order to raise sacrifice corrosion prevention ability further, since it is larger than Sn for whether your being Haruka, the corrosion resistance of the plating layer itself will be spoiled for the elution of Zn itself. This invention solves the above-mentioned technical problem, balances corrosion resistance, workability, and weldability highly, and offers the melting Sn system plating steel plate which does not use Pb.

[0006]

[Means for Solving the Problem] For the purpose of offering the rust-proofing steel plate in which the cut section and an end face carried out improvement in rust-proofing ability excluding Pb, this invention persons consider various a plating presentation, coat structures, configurations, etc., and result in this invention. This invention relates to the rust-proofing steel plate for fuel tanks excellent in the workability characterized by the major-axis dimension of the plating metallic crystal in the maximum front face having a plating organization 20.0mm or less, and corrosion resistance through an alloy layer with a thickness of 3.0 micrometers or less in the Sn-Mg alloy-plating steel plate containing 0.1 - 4% of Mg.

[0007] Furthermore, when it contains 0.5 - 20% of Zn, and 0.01 - 2% of calcium in a plating layer and contains one sort of nickel, Co, and Cu, or two sorts or more in this 0.5% or more alloy layer, it is related with the rust-proofing steel plate for fuel tanks excellent in the workability characterized by having the after-treatment layer which consists of an inorganic compound, an organic compound, or its composite on the maximum front face, and corrosion resistance.

[0008] This invention is explained below at a detail. Plating is performed after pretreating removal of rolling oil or an oxide film etc. by making into galvanized material the steel plate [ finishing / annealing ] which passed the steel cast piece through a series of processes, such as hot rolling, acid washing, cold rolling, annealing, and temper rolling, and rolled stock. It is necessary to be the component system which controls progress of the corrosion in that it is the component system which can process the complicated configuration of a fuel tank about a steel component, that the thickness of the alloy layer of a steel-plating layer interface can prevent plating exfoliation thinly, the interior of a fuel tank, and an external environment.

[0009] It is desirable to perform a Sn-Mg alloy plating by the hot-dipping method in this invention. The greatest reason nil why a hot-dipping method is desirable is because the direction of a hot-dipping method is suitable for reservation of plating coating weight. If long duration is electrolyzed also with electroplating, although plating coating weight is securable, it is not economical. The plating coating weight range aimed at by this invention is the field of thick eyes comparatively, and its hot-dipping method is as the optimal as 20-150g/m<sup>2</sup> (one side). Furthermore, since controlling a presentation appropriately is accompanied by difficulty when the potential difference of a plating element is large, a Sn-Mg alloy has the optimal hot-dipping method.

[0010] Next, although it is the reason for limitation of a plating presentation, it limits by corrosion resistance balance in a gas-tank inside and external surface. Since perfect rust-proofing capacity is needed, tank external surface is painted after tank shaping. Therefore, although paint thickness determines rust-proofing capacity, the rust prevention effectiveness is so large that there is much Mg coating weight in a plating layer as a material.

[0011] On the other hand, only in the case of a normal gasoline, the corrosion in a tank inside does not pose a problem, but quite intense corrosive environment appears by mixing of water, mixing of a chlorine ion, generation of the organic carboxylic acid by the oxidation degradation of a gasoline, etc. When a gasoline leaks to the tank exterior by punching corrosion, there is a possibility of leading to a major accident and these corrosion must be prevented completely. When the degradation gasoline containing the above-mentioned corrosion promotion component was produced and the engine performance under [ various ] conditions was investigated, it was checked that the Sn-Mg alloy-plating coat which contains Mg 4% or less demonstrates the extremely excellent corrosion resistance.

[0012] Since a plating metal does not have sacrifice corrosion prevention ability to a ferrite when pure Sn or Mg content which does not contain Mg at all is less than 0.1%, in a tank inside, early rust generating poses a problem in pitting in the plating pinhole section, and tank external surface. Since Mg dissolves preferentially and a corrosion product is generated so much for a short period of time when Mg is contained so much exceeding 4%, there are a lifting and a cone problem about the blinding of a carburetor. Moreover, when Mg content increases, the workability of a plating layer also falls. When Mg content furthermore increases, solder nature falls sharply.

[0013] Therefore, as for Mg content in the Sn-Mg alloy plating in this invention, it is desirable to acquire 0.1 - 4% of range and further more sufficient sacrifice corrosion prevention operation, to control

the dissolution of Mg, and to carry out in 0.2 - 2% of range for carrying out that it is harder to start the blinding of a carburetor. Although rust-proofing ability improves by addition of Mg, 0.5 - 20% of Zn and 0.01 - 2% of calcium may be added further. Addition of Zn lowers the potential of a plating layer and gives sacrifice corrosion prevention ability. For that purpose, 0.5% or more of addition is desirable, and superfluous addition causes a melting point rise, and since it leads to superfluous growth of the intermetallic-compound layer of a plating lower layer, it may be 20% or less. calcium contributes to the improvement in rust-proofing ability like Mg. However, since the contribution to the rise of the melting point is also large, it is preferably [ too ] desirable 0.01 - 2% of to add to an excess.

[0014] In a hot-dipping method, formation of an alloy layer is unavoidable. It is because what a galvanized front face and a plating metal are [ a thing ] well damp (it alloys) is important in order to prevent generating of a plating pinhole and to obtain a plating coat with uniform and good corrosion resistance. In order to process a complicated configuration like a fuel tank, it is necessary to secure advanced workability. Although little generation of the alloy layer must be carried out in order to get wet well, since it is hard and weak, when it tends to produce a crack at the time of processing and becomes thicker than a certain thickness, a crack will spread it in the plating layer of an alloy layer outside, it will produce a crack in a plating layer, and causes plating exfoliation and corrosion-resistant degradation by the damage of a plating layer. Such plating exfoliation needs to have a plating kind, thickness and a steel type, and very big relation, and when it is this invention, the thickness of an alloy layer needs to be 3.0 micrometers or less.

[0015] For a wettability improvement, it is also effective to change a steel plate front face. In the production process of a steel plate, it is hard to remove the oxide formed in a steel plate front face, and it checks plating nature. In order to eliminate this effect, nickel, Co, Cu, etc. which are easy to react with tin to the steel plate front face in front of plating are galvanized, and wettability is improved. nickel, Co, Cu, etc. may be galvanized alone and may be an alloy with Fe, or the alloy of these metals. As an amount of plating, it is wrap extent 2, for example, 0.1 - 2.0 g/m, to homogeneity about a steel plate front face. Extent is enough. As a product after plating, the rust-proofing steel plate excellent in workability and corrosion resistance can be obtained by containing one sort of nickel, Co, and Cu, or two sorts or more in 0.5% or more alloy layer.

[0016] Sn is a subject and, as for the plating layer in this invention, Mg exists in it. This Sn and Mg are galvanized on a steel plate front face in the state of melting, and are divided into Sn and a Mg<sub>2</sub>Sn phase in a cooling process. The case where are by the way and Sn crystallizes as a primary phase bordering on the point at the time of cooling and Mg<sub>2</sub>Sn of about 2%Mg may crystallize the eutectic point as a primary phase. The engine performance of a plating steel plate is greatly influenced by the formation condition of the crystal in a cooling process, i.e., how to solidify. The condition of solidification of a plating crystal is observable with the naked eye by corroding the front face after plating lightly with weak acid or weak alkali.

[0017] Generally, the small crystalline structure (the crystalline structure is called a spangle below) appears, when forced cooling of the degree of pole is performed, but since it builds in a big distortion during an organization, corrosion resistance and workability may be inferior in it. On the other hand, if it cools gently after plating, a big spangle will be formed and the problem of heat distortion will be lost. However, in a Sn-Mg alloy plating, Mg<sub>2</sub>Sn may grow greatly. Since such a plating coat shows the inclination only for Mg to be quickly dissolved in corrosive environment and it becomes impossible to expect the long-term corrosion prevention operation by Mg, it makes corrosion resistance deteriorate as a result. Moreover, since a Mg<sub>2</sub>Sn crystal serves as an origin of crack initiation also at the time of processing, it is not desirable. Since it is such, in this invention, it is using to add a limit to the magnitude of a spangle as main invention components.

[0018] The major-axis die length of a crystal can define the magnitude of a spangle. Usually, although the round spangle was formed in many cases, since the major-axis die length and minor-axis die length of a crystal were not necessarily equal, it decided to define by this invention with the major-axis die length of a crystal. In this invention, it is more nearly required than the viewpoint of corrosion resistance and workability as a spangle after plating for the major-axis die length of a crystal to cost 20mm or less

for a spangle 10mm or less still more desirably. Since a Mg<sub>2</sub> Sn crystal tends to grow greatly as the major-axis die length of a crystal mentioned above as the big and rough crystal 20mm or more, and the dissolution of rapid Mg or Mg<sub>2</sub> Sn serves as an origin of the crack initiation at the time of processing, it is not desirable.

[0019] Since, as for a fine crystal 1.0mm or less, the major-axis die length of a crystal builds in a big heat distortion during an organization, it is worried, but heat, such as paint baking, is applied in the process processed as that Mg<sub>2</sub> Sn is extremely distributed by homogeneity and a fuel tank, and since disconnection of distortion is expected, the engine performance which was excellent as practicality ability is expected. Therefore, it is not necessary to set up especially the minimum dimension of a spangle. In this invention, thoroughgoing corrosion resistance is expected by performing after treatment which consists a plating layer front face of an inorganic compound, an organic compound, or its composite further. This processing has the effectiveness which the Sn-Mg plating layer of a substrate has very good familiarity, and covers defective parts, such as a minute pinhole, or is made to dissolve a plating layer, and restores a pinhole, and raises corrosion resistance sharply.

[0020]

[Example] An example shows the quality characteristic of the rust-proofing steel plate for fuel tanks of this invention.

(Example 1) Mg was introduced into the Sn-Mg plating bath (temperature of 350 degrees C) included 1.5% after applying the flux for plating which contains a zinc chloride and a hydrochloric acid for a steel plate [ finishing / annealing of 0.8mm of board thickness, and pressure regulation ]. From the plating bath and the post-plating bath to which the steel plate front face was made to fully react, the steel plate was pulled out, and coating weight preparation was performed by the gas wiping method, and it cooled quickly. The steel plate after plating is 0.7-micrometer FeSn<sub>2</sub>. It was what has the alloy layer, the coating weight (total coating weight of Sn+Mg) of 32g/the plating layer of m<sup>2</sup> (per one side) made into a subject. They are 15 mg/m<sup>2</sup> as chromium on this front face. Chromate treatment of coating weight was performed and it considered as the product plate.

[0021] In order to question the crystalline structure of this steel plate, when the hydrochloric acid corroded the front face lightly 1%, the crystalline structure accepted with the naked eye appeared, and the average of that major-axis dimension was 6.5mm. After cross-section polish, when the distribution condition of Sn and Mg was analyzed in EPMA (electron probe microanalyzer), the uniform distribution condition was checked. In the pressurized container, 10vol(s)% water was added to the compulsive degradation gasoline left at 100 degrees C one whole day and night, and etching fluid was produced. When the 45 degree-Cx3 week corrosion test was performed in this etching fluid, the eluted metal ion was judged to be what shows good corrosion resistance, although Mg is a subject and 2000 ppm elution was accepted.

[0022] (Example 2) They are 0.8 g/m<sup>2</sup> to a steel plate [ finishing / annealing of 0.8mm of board thickness, and pressure regulation ]. Electric nickel plating of coating weight was performed, and Mg was introduced into the Sn-Mg plating bath (temperature of 350 degrees C) included 3% after applying the flux for plating containing a zinc chloride and a hydrochloric acid. From the plating bath and the post-plating bath to which the steel plate front face was made to fully react, the steel plate was pulled out, and coating weight preparation was performed by the gas wiping method, and it cooled quickly. The steel plate after plating is 0.5-micrometer FeSn<sub>2</sub>. It was what has the alloy layer (17% of nickel content) and the plating layer of coating weight (total coating weight of Sn+Mg) 33 g/m<sup>2</sup> (per one side) which are made into a subject. They are 12 mg/m<sup>2</sup> as chromium on this front face. Chromate treatment of coating weight was performed and it considered as the product plate.

[0023] In order to question the crystalline structure of this steel plate, when the hydrochloric acid corroded the front face lightly 1%, the crystalline structure accepted with the naked eye appeared, and the average of that major-axis dimension was 12.0mm. After cross-section polish, although a little big Mg<sub>2</sub> Sn crystal was somewhat observed compared with the example 1 when the distribution condition of tin and zinc was analyzed in EPMA (electron probe microanalyzer), the almost good distribution condition was checked. In the pressurized container, 10vol(s)% water was added to the compulsive

degradation gasoline left at 100 degrees C one whole day and night, and etching fluid was produced. When the 45 degree-Cx3 week corrosion test was performed in this etching fluid, the eluted metal ion was judged to be what shows good corrosion resistance, although Mg is a subject and 3000 ppm elution was accepted.

[0024] (Example 3) They are 0.8 g/m<sup>2</sup> to a steel plate [ finishing / annealing of 0.8mm of board thickness, and pressure regulation ]. Electric nickel plating of coating weight was performed, and Mg was introduced into the Sn-Mg plating bath (temperature of 400 degrees C) included 2% after applying the flux for plating containing a zinc chloride and a hydrochloric acid. From the plating bath and the post-plating bath to which the steel plate front face was made to fully react, the steel plate was pulled out, and coating weight preparation was performed by the gas wiping method, and it cooled quickly. The steel plate after plating is 0.7-micrometer FeSn<sub>2</sub>. It was what has the alloy layer (12% of nickel content) and the plating layer of coating weight (total coating weight of Sn+Mg) 30 g/m<sup>2</sup> (per one side) which are made into a subject. They are 10 mg/m<sup>2</sup> as chromium on this front face. What performed chromate treatment of coating weight, and the non-processed material which does not perform chromate treatment were produced. When the same corrosion test as examples 1 and 2 was performed about two kinds of this steel plate, non-processed material was accepted as it is better for chromate treatment material to perform after treatment for accepting 4700 ppm Mg elution compared with 2100 ppm Mg elution, and expecting corrosion-resistant improvement further.

[0025] (Example 4) They are 0.3 g/m<sup>2</sup> to a steel plate [ finishing / annealing of 0.8mm of board thickness, and pressure regulation ]. Electric cobalt plating of coating weight was performed, and Mg was introduced into the tinning bath (temperature of 340 degrees C) included 1% after applying the flux for plating containing a zinc chloride and a hydrochloric acid. From the plating bath and the post-plating bath to which the steel plate front face was made to fully react, the steel plate was pulled out, and coating weight preparation was performed by the gas wiping method, and it cooled quickly. The steel plate after plating is 0.5-micrometer FeSn<sub>2</sub>. It was what has the alloy layer (7% of cobalt content) and the plating layer of coating weight (total coating weight of Sn+Mg) 35 g/m<sup>2</sup> (per one side) which are made into a subject. They are 12 mg/m<sup>2</sup> as chromium on this front face. Chromate treatment of coating weight was performed and it considered as the product plate. When the same corrosion test as examples 1 and 2 was performed about this steel plate, the elution metal ion showed 1800 ppm and good corrosion resistance.

[0026] (Example 5) They are 0.6 g/m<sup>2</sup> to a steel plate [ finishing / annealing of 0.8mm of board thickness, and pressure regulation ]. Electrolytic copper plating of coating weight was performed, and Mg was introduced into the Sn-Mg plating bath (concentration of 360 degrees C) included 1.5% after applying the flux for plating containing a zinc chloride and a hydrochloric acid. From the plating bath and the post-plating bath to which the steel plate front face was made to fully react, the steel plate was pulled out, and coating weight preparation was performed by the gas wiping method, and it cooled quickly. The steel plate after plating was what has the alloy layer (10% of copper content) and the plating layer of coating weight (total coating weight of Sn+Mg) 45 g/m<sup>2</sup> (per one side) which make 0.6-micrometer FeSn<sub>2</sub> a subject. They are 18 mg/m<sup>2</sup> as chromium on this front face. Chromate treatment of coating weight was performed and it considered as the product plate. When the same corrosion test as examples 1 and 2 was performed about this steel plate, the elution metal ion showed 1400 ppm and good corrosion resistance.

[0027] (Example 6) After applying the flux for plating which contains a zinc chloride and a hydrochloric acid for a steel plate [ finishing / annealing of 0.8mm of board thickness, and pressure regulation ], Mg was introduced into the Sn-Mg-Zn plating bath (temperature of 350 degrees C) which contains Zn 8% 1.5%. From the plating bath and the post-plating bath to which the steel plate front face was made to fully react, the steel plate was pulled out, and coating weight preparation was performed by the gas wiping method, and it cooled quickly. The steel plate after plating is 0.7-micrometer FeSn<sub>2</sub>. It was what has the alloy layer and the plating layer of coating weight (total coating weight of Sn+Mg+Zn) 32 g/m<sup>2</sup> (per one side) which are made into a subject. They are 15 mg/m<sup>2</sup> as chromium on this front face. Chromate treatment of coating weight was performed and it considered as the product plate.



[0028] In order to question the crystalline structure of this steel plate, when the hydrochloric acid corroded the front face lightly 1%, the crystalline structure accepted with the naked eye appeared, and the average of that major-axis dimension was 6mm. After cross-section polish, when the distribution condition of Sn, and Mg and Zn was analyzed in EPMA (electron probe microanalyzer), the uniform distribution condition was checked. In the pressurized container, 10vol(s)% water was added to the compulsive degradation gasoline left at 100 degrees C one whole day and night, and etching fluid was produced. When the 45 degree-Cx3 week corrosion test was performed in this etching fluid, the eluted metal ion was judged to be what shows good corrosion resistance, although Mg and Zn are subjects and 2100 ppm elution was accepted in total.

[0029] (Example 1 of a comparison) Coating weight 40 g/m<sup>2</sup> of the terne sheet (lead-tin alloy plating steel plate) currently conventionally used as a gas-tank ingredient When the same corrosion test as an example was presented with the ingredient, it turned out that 9700 ppm and 1200 ppm of iron are eluted, and lead is inferior to this invention steel plate.

[0030] (Example 2 of a comparison) By the same procedure as an example 2, they are 0.8 g/m<sup>2</sup> to a steel plate [ finishing / annealing of 0.8mm of board thickness, and pressure regulation ]. Electric nickel plating of coating weight was performed, and Mg was introduced into the tinning bath (temperature of 350 degrees C) included 1.5% after applying the flux for plating containing a zinc chloride and a hydrochloric acid. From the plating bath and the post-plating bath to which the steel plate front face was made to fully react, the steel plate was pulled out, coating weight preparation was performed by the gas wiping method, and garadual cooling was carried out. The steel plate after plating is 0.5-micrometer FeSn<sub>2</sub>. It was what has the alloy layer (17% of nickel content) and the plating layer of coating weight (total coating weight of Sn+Mg) 33 g/m<sup>2</sup> (per one side) which are made into a subject. They are 12 mg/m<sup>2</sup> as chromium on this front face. Chromate treatment of coating weight was performed and it considered as the product plate.

[0031] In order to question the crystalline structure of this steel plate, when the hydrochloric acid corroded the front face lightly 1%, the big crystal grew by garadual cooling and the average of that major-axis dimension was 30.0mm. After cross-section polish, when the distribution condition of Sn and Mg was analyzed in EPMA (electron probe microanalyzer), compared with the example 2, much needlelike huge Mg<sub>2</sub> Sn crystals were observed, and the segregation condition of Sn and Mg was checked. As a result of the same corrosion test as an example 2, 5200 ppm Mg elution was accepted and corrosion-resistant degradation by the huge Mg<sub>2</sub> Sn crystal was accepted.

[0032]

[Effect of the Invention] By this invention, it excelled in corrosion resistance, workability, and weldability, and the lead free rust-proofing steel plate for fuel tanks borne also to a degradation gasoline etc. for a long period of time was obtained.

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(54) 【発明の名称】 溶融Sn-Mg系めっき鋼板

(57) 【要約】

【課題】 優れた耐食性を有し、特に自動車燃料タンク材料として好適なPbフリーの溶融Sn-Mg系めっきを提供する。

【解決手段】 0.1~4%のMgを含み、最表面におけるめっき金属結晶の長径寸法が20.0mm以下のめっき組織を有することを特徴とする溶融Sn-Mg系鋼板。更には、Zn0.5~20%、Ca0.01~2%をめっき層に含有する場合、Ni、Co、Cuを合金層中に含有する場合、無機化合物あるいは有機化合物またはその複合物よりなる後処理層を最表面に有する場合がある。

【効果】 該めっき鋼板は、Pbを使用しない燃料タンク材料として好適な特性を有する。

## 【特許請求の範囲】

【請求項1】 鋼板表面に、厚み3.0 $\mu$ m以下の合金層を有し、その表面に組成が質量%で、Mgを0.1~4%含有し残部がSnと不可避的不純物からなり、かつ最表面におけるめっき金属結晶の長径寸法が20mm以下のめっき層を有することを特徴とする溶融Sn-Mg系めっき鋼板。

【請求項2】 鋼板表面に溶融Sn-Mgめっき層を有し、めっき層の組成が質量%で74~99.9%のSnを含有することを特徴とする請求項1に記載の溶融Sn-Mg系めっき鋼板。

【請求項3】 めっき層の組成がSn、Mgに加え、重量%でZn0.5~20%、Ca0.01~2%の1種または2種以上を含有することを特徴とする請求項1または2に記載の溶融Sn-Mg系めっき鋼板。

【請求項4】 鋼板表面に、Ni、Co、Cuの1種または2種以上を合計で0.5%以上含有する厚み3.0 $\mu$ m以下の合金層を有し、その表面に組成が質量%でMgを0.1~4%含有し残部がSnと不可避的不純物からなりかつ最表面におけるめっき金属結晶の長径寸法が20mm以下のめっき層を有することを特徴とする請求項1~3いずれかに記載の溶融Sn-Mg系めっき鋼板。

【請求項5】 めっき層表面に、無機化合物あるいは有機化合物、またはその複合物よりなる後処理層を有することを特徴とする請求項1~4いずれかに記載の溶融Sn-Mg系めっき鋼板。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】本発明は、優れた耐食性、接合性、加工性を兼備し、自動車燃料タンク材料、家庭用電気機械、産業機械材料として好適な溶融Sn-Mg系めっき鋼板に関するものである。

## 【0002】

【従来の技術】従来、燃料タンク材料としてこれまで耐食性、加工性、はんだ性（溶接性）等の優れたPb-Sn合金めっき鋼板が主として用いられ、自動車用燃料タンクとして幅広く使用されている。一方、Sn-Zn合金めっき鋼板は、例えば特開昭52-130438号公報に開示されたように、ZnおよびSnイオンを含む水溶液中で電解する電気めっき法で主として製造されてきた。Snを主体とするSn-Zn合金めっき鋼板は、耐食性やはんだ性に優れており電子部品などに多く使用されている。一方、自動車燃料タンク用途でこのSn-Znめっき鋼板が優れた特性を有することが知見され、特開平8-269733号公報、特開平8-269734号公報等において、めっき組織を制御した溶融Sn-Znめっき鋼板が開示されている。

## 【0003】

【発明が解決しようとする課題】自動車用燃料タンク素

材として使用されてきたPb-Sn合金めっき鋼板は、各種の優れた特性（例えば、加工性、タンク内面耐食性、はんだ性、シーム溶接性等）が認められ愛用されてきたが、近年の地球環境認識の高まりにつれPbフリー化の方向に移行しつつある。一方、Sn-Zn電気合金めっき鋼板は、主としてはんだ性等の要求される電子部品として腐食環境がさほど厳しくない用途で使用されてきた。

【0004】前記した溶融Sn-Znめっき鋼板は、確かに優れた耐食性、加工性、半田性を有するものである。しかし、近年、更なる耐食性の向上が求められており、Sn-Znめっき鋼板では巾の狭いカット部（地鉄まで達するような疵）の犠牲防食効果はある程度あるものの、カット部の巾が広い場合や、めっきが被覆されていない端部では犠牲防食能が十分に発揮されない。

【0005】特に、塩害環境を想定した塩水噴霧試験では赤錆発生に至るまでの期間が短く、十分とはいえない。犠牲防食能を更に向上させるためにはZnの添加量を増やせばよいのであるが、Zn量が高くなりすぎるとめっき層の主体がSnからZnへと移行していき、Zn自体の溶出がSnよりも遙かに大きいため、めっき層自体の耐食性が損なわれる。本発明は、上記の課題を解決し、耐食性、加工性、溶接性を高度にバランスし、Pbを使用しない溶融Sn系めっき鋼板を提供するものである。

## 【0006】

【課題を解決するための手段】本発明者らは、Pbを含まず、カット部、端面の防錆能向上させた防錆鋼板を提供することを目的に、めっき組成・皮膜構造・構成等を種々検討し、本発明に至ったものである。本発明は、0.1~4%のMgを含むSn-Mg合金めっき鋼板において、3.0 $\mu$ m以下の厚みの合金層を介して、最表面におけるめっき金属結晶の長径寸法が20.0mm以下のめっき組織を有することを特徴とする加工性、耐食性に優れた燃料タンク用防錆鋼板に関するものである。

【0007】更には、Zn0.5~20%、Ca0.01~2%をめっき層に含有する場合、Ni、Co、Cuの1種または2種以上を、0.5%以上該合金層中に含有する場合、あるいは、無機化合物あるいは有機化合物、またはその複合物よりなる後処理層を最表面に有する場合があることを特徴とする加工性、耐食性に優れた燃料タンク用防錆鋼板に関するものである。

【0008】以下に本発明について詳細に説明する。鋼箔片を熱間圧延・酸洗・冷間圧延・焼鈍・調質圧延等の一連の工程を経た焼鈍済みの鋼板、また圧延材を被めっき材として、圧延油あるいは酸化膜の除去等の前処理を行った後、めっきを行う。鋼成分については、燃料タンクの複雑な形状に加工できる成分系であること、鋼-めっき層界面の合金層の厚みが薄くめっき剥離を防止できること、燃料タンク内部および外部環境における腐食の

進展を抑制する成分系である必要がある。

【0009】本発明では、Sn-Mg合金めっきは溶融めっき法で行うのが望ましい。溶融めっき法が望ましい最大の理由は、めっき付着量の確保には溶融めっき法の方が適しているためである。電気めっき法でも長時間の電解を行えばめっき付着量は確保できるが、経済的ではない。本発明で狙うめっき付着量範囲は、 $20 \sim 150 \text{ g/m}^2$  (片面)と比較的厚目付の領域であり、溶融めっき法が最適である。さらに、めっき元素の電位差が大きい場合、適切に組成を制御することは困難を伴うため、Sn-Mg合金は溶融めっき法が最適である。

【0010】次にめっき組成の限定理由であるが、ガソリンタンク内面と外面における耐食性のバランスにより限定したものである。タンク外面は、完璧な防錆能力が必要とされるためタンク成形後に塗装される。したがって、塗装厚みが防錆能力を決定するが、素材としてはめっき層中のMg付着量が多いほど赤錆防止効果が大きい。

【0011】一方、タンク内面での腐食は、正常なガソリンのみの場合には問題とならないが、水の混入、塩素イオンの混入、ガソリンの酸化劣化による有機カルボン酸の生成等により、かなり激しい腐食環境が出現する。もし、穿孔腐食によりガソリンがタンク外部に漏れた場合、重大事故につながる恐れがあり、これらの腐食は完全に防止されねばならない。上記の腐食促進成分を含む劣化ガソリンを作製し、各種条件下での性能を調べたところ、Mgを4%以下含有するSn-Mg合金めっき皮膜は極めて優れた耐食性を発揮することが確認された。

【0012】Mgを全く含まない純SnまたはMg含有量が0.1%未満の場合、めっき金属が地鉄に対し犠牲防食能を持たないため、タンク内面ではめっきピンホール部での孔食、タンク外面では早期の赤錆発生が問題となる。Mgが4%を超えて多量に含まれる場合、Mgが優先的に溶解し、腐食生成物が短期間に多量に発生するため、キャブレターの目詰まりを起こしやすい問題がある。また、Mg含有量が多くなることによってめっき層の加工性も低下する。さらにMg含有量が多くなることによってはんだ性が大幅に低下する。

【0013】したがって、本発明におけるSn-Mg合金めっきにおけるMg含有量は、0.1~4%の範囲、更に、より十分な犠牲防食作用を得、Mgの溶解を抑制してキャブレターの目詰まりをより起こしにくくするには0.2~2%の範囲にすることが望ましい。Mgの添加で防錆能は向上するが、更にZn0.5~20%、Ca0.01~2%を添加してもよい。Znの添加はめっき層の電位を下げ、犠牲防食能を付与する。そのためには0.5%以上の添加が望ましく、過剰な添加は融点上昇をひきおこし、めっき下層の金属間化合物層の過剰な成長につながるため20%以下とする。Caは、Mg同様に防錆能向上に寄与する。しかしながら、融点の上昇

に対する寄与も大きいため過剰に添加することはやはり好ましくなく0.01~2%が望ましい。

【0014】溶融めっき法においては、合金層の形成を避けることはできない。めっきピンホールの発生を防止し均一で耐食性良好なめっき皮膜を得るためには、被めっき表面とめっき金属が良く濡れる(合金化する)ことが重要であるからである。燃料タンクのように複雑な形状に加工するためには、高度の加工性を確保する必要がある。合金層は、良く濡れるためには少量生成しなければならないが、硬くて脆いために加工時にクラックを生じ易く、ある厚みよりも厚くなると合金層外側のめっき層にクラックが伝播しめっき層中に割れを生ずることになり、めっき剥離やめっき層のダメージによる耐食性劣化の原因となる。このようなめっき剥離は、めっき種・厚み・鋼種と非常に大きな関連があり、本発明の場合、合金層の厚みは $3.0 \mu\text{m}$ 以下である必要がある。

【0015】濡れ性の改善のためには、鋼板表面を変化させることも有効である。鋼板の製造工程において、鋼板表面に形成される酸化物は除去しにくいものであり、めっき性を阻害する。この影響を排除するため、めっき直前の鋼板表面に錫と反応しやすいNi、Co、Cu等をめっきし、濡れ性を改善する。Ni、Co、Cu等は単体でめっきしても良いし、Feとの合金、あるいはこれらの金属同士の合金であっても良い。めっき量としては鋼板表面を均一に覆う程度、例えば $0.1 \sim 2.0 \text{ g/m}^2$ 程度で十分である。めっき後の製品としては、Ni、Co、Cuの1種または2種以上を0.5%以上合金層中に含有することで加工性、耐食性に優れた防錆鋼板を得ることができる。

【0016】本発明におけるめっき層はSnが主体であり、その中にMgが存在する。このSnおよびMgは、溶融状態にて鋼板表面にめっきされ、冷却過程にてSnおよびMg<sub>2</sub>Sn相に分離する。共晶点は約2%Mgのところであり、その点を境にして、冷却当初にSnが初晶として晶出する場合と、Mg<sub>2</sub>Snが初晶として晶出する場合がある。めっき鋼板の性能は、冷却過程における結晶の形成具合すなわちかたまり方に大きく左右される。めっき結晶の固化の状態は、めっき後の表面を弱酸あるいは弱アルカリで軽く腐食することにより肉眼にて観察することができる。

【0017】一般的には小さな結晶組織(結晶組織を以下スバンクルと称す)は、極度の急速冷却を行った場合に出現するが、大きな歪みを組織中に内蔵するため耐食性と加工性の劣る場合がある。一方、めっき後緩やかに冷却すると、大きなスバンクルが形成され、熱歪みの問題はなくなる。しかし、Sn-Mg合金めっきにおいては、Mg<sub>2</sub>Snが大きく成長してしまう場合もある。このようなめっき皮膜は、腐食環境中にてMgのみ急速に溶解される傾向を示し、Mgによる長期の防食作用が期待できなくなるため、結果的には耐食性を劣化させるこ

となる。また、加工時にも、 $Mg_2Sn$ 結晶がクラック発生の起点となるため好ましくない。このような理由から、本発明ではスパンクルの大きさに制限を加えることを主要な発明構成要素としている。

【0018】スパンクルの大きさは、結晶の長径長さにより定義することができる。通常、丸いスパンクルが形成されることが多いが、必ずしも結晶の長径長さと同径長さは等しくないため、本発明では結晶の長径長さにより定義することにした。本発明では、耐食性、加工性の観点より、めっき後のスパンクルとして、結晶の長径長さが20mm以下、更に望ましくは10mm以下のスパンクルとすることが必要である。結晶の長径長さが20mm以上の粗大結晶では、前述したごとく $Mg_2Sn$ 結晶が大きく成長しやすく、急速なMgの溶解あるいはMg<sub>2</sub>Snが加工時のクラック発生の起点となるために好ましくない。

【0019】結晶の長径長さが1.0mm以下の微細結晶は大きな熱歪みを組織中に内蔵するため心配されるが、 $Mg_2Sn$ が極めて均一に分散されていることおよび燃料タンクとして加工される過程にて塗装焼き付け等の熱が加えられ、歪みの開放が期待されるため実用性能としては優れた性能が期待される。したがって、スパンクルの下限寸法を特に設定する必要はない。本発明では、めっき層表面を更に無機化合物あるいは有機化合物、またはその複合物よりなる後処理を行うことにより万全の耐食性が期待される。この処理は下地のSn-Mgめっき層とは非常に馴染みが良く、微小ピンホール等の欠陥部を被覆したり、めっき層を溶解させピンホールを修復する効果があり耐食性を大幅に向上させる。

【0020】

【実施例】本発明の燃料タンク用防錆鋼板の品質特性を実施例で示す。

（実施例1）板厚0.8mmの焼鈍、調圧済みの鋼板を、塩化亜鉛及び塩酸を含むめっき用フラックスを塗布した後、Mgを1.5%含むSn-Mgめっき浴（温度350℃）に導入した。めっき浴と鋼板表面を十分に反応させた後めっき浴より鋼板を引き出し、ガスワイピング法により付着量調整を行い急速冷却した。めっき後の鋼板は、0.7μmのFeSn<sub>2</sub>を主体とする合金層と付着量（Sn+Mgの全付着量）32g/m<sup>2</sup>（片面あたり）のめっき層を有するものであった。この表面上にクロムとして15mg/m<sup>2</sup>の付着量のクロメート処理を行い製品板とした。

【0021】この鋼板の結晶組織を調べるため、1%塩酸で表面を軽く腐食したところ肉眼で認められる結晶組織が現れ、その長軸寸法の平均値は6.5mmであった。断面研磨後、SnとMgの分布状態をEPMA（電子プローブマイクロアナライザー）にて分析したところ、均一な分布状態が確認された。圧力容器中にて、100℃で一昼夜放置した強制劣化ガソリンに10vol

%の水を添加し腐食液を作製した。この腐食液中にて、45℃×3週間の腐食試験を行ったところ、溶出した金属イオンはMgが主体であり、2000ppmの溶出が認められたが、良好な耐食性を示すものと判断された。

【0022】（実施例2）板厚0.8mmの焼鈍、調圧済みの鋼板に0.8g/m<sup>2</sup>の付着量の電気ニッケルめっきを施し、塩化亜鉛及び塩酸を含むめっき用フラックスを塗布した後、Mgを3%含むSn-Mgめっき浴（温度350℃）に導入した。めっき浴と鋼板表面を十分に反応させた後めっき浴より鋼板を引き出し、ガスワイピング法により付着量調整を行い急速冷却した。めっき後の鋼板は、0.5μmのFeSn<sub>2</sub>を主体とする合金層（17%のNi含有）と付着量（Sn+Mgの全付着量）33g/m<sup>2</sup>（片面あたり）のめっき層を有するものであった。この表面上にクロムとして12mg/m<sup>2</sup>の付着量のクロメート処理を行い製品板とした。

【0023】この鋼板の結晶組織を調べるため、1%塩酸で表面を軽く腐食したところ肉眼で認められる結晶組織が現れ、その長軸寸法の平均値は12.0mmであった。断面研磨後、錫と亜鉛の分布状態をEPMA（電子プローブマイクロアナライザー）にて分析したところ、実施例1に比べやや大きな $Mg_2Sn$ 結晶が多少観察されたが、ほぼ良好な分布状態が確認された。圧力容器中にて、100℃で一昼夜放置した強制劣化ガソリンに10vol%の水を添加し腐食液を作製した。この腐食液中にて、45℃×3週間の腐食試験を行ったところ、溶出した金属イオンはMgが主体であり、3000ppmの溶出が認められたが、良好な耐食性を示すものと判断された。

【0024】（実施例3）板厚0.8mmの焼鈍、調圧済みの鋼板に0.8g/m<sup>2</sup>の付着量の電気ニッケルめっきを施し、塩化亜鉛及び塩酸を含むめっき用フラックスを塗布した後、Mgを2%含むSn-Mgめっき浴（温度400℃）に導入した。めっき浴と鋼板表面を十分に反応させた後めっき浴より鋼板を引き出し、ガスワイピング法により付着量調整を行い急速冷却した。めっき後の鋼板は、0.7μmのFeSn<sub>2</sub>を主体とする合金層（12%のNi含有）と付着量（Sn+Mgの全付着量）30g/m<sup>2</sup>（片面あたり）のめっき層を有するものであった。この表面上にクロムとして10mg/m<sup>2</sup>の付着量のクロメート処理を行ったものと、クロメート処理を行わない無処理材を作製した。この2種類の鋼板につき、実施例1および2と同様の腐食試験を行ったところ、クロメート処理材は2100ppmのMg溶出に比べ、無処理材は4700ppmのMg溶出が認められ、更に耐食性向上を期するには後処理を行ったほうがよいと認められた。

【0025】（実施例4）板厚0.8mmの焼鈍、調圧済みの鋼板に0.3g/m<sup>2</sup>の付着量の電気コバルトめっきを施し、塩化亜鉛及び塩酸を含むめっき用フラック

スを塗布した後、Mgを1%含む錫めっき浴（温度340℃）に導入した。めっき浴と鋼板表面を十分に反応させた後めっき浴より鋼板を引き出し、ガスワイピング法により付着量調整を行い急速冷却した。めっき後の鋼板は、0.5μmのFeSn<sub>2</sub>を主体とする合金層（7%のコバルト含有）と付着量（Sn+Mgの全付着量）35g/m<sup>2</sup>（片面あたり）のめっき層を有するものであった。この表面上にクロムとして12mg/m<sup>2</sup>の付着量のクロメート処理を行い製品板とした。この鋼板につ

き、実施例1および2と同様の腐食試験を行ったところ、溶出金属イオンは1800ppmと良好な耐食性を示した。  
 【0026】（実施例5）板厚0.8mmの焼鈍、調圧済みの鋼板に0.6g/m<sup>2</sup>の付着量の電気銅めっきを施し、塩化亜鉛及び塩酸を含むめっき用フラックスを塗布した後、Mgを1.5%含むSn-Mgめっき浴（濃度360℃）に導入した。めっき浴と鋼板表面を十分に反応させた後めっき浴より鋼板を引き出し、ガスワイピング法により付着量調整を行い急速冷却した。めっき後の鋼板は、0.6μmのFeSn<sub>2</sub>を主体とする合金層（10%の銅含有）と付着量（Sn+Mgの全付着量）45g/m<sup>2</sup>（片面あたり）のめっき層を有するものであった。この表面上にクロムとして18mg/m<sup>2</sup>の付着量のクロメート処理を行い製品板とした。この鋼板につ

き、実施例1および2と同様の腐食試験を行ったところ、溶出金属イオンは1400ppmと良好な耐食性を示した。  
 【0027】（実施例6）板厚0.8mmの焼鈍、調圧済みの鋼板を、塩化亜鉛及び塩酸を含むめっき用フラックスを塗布した後、Mgを1.5%、Znを8%含むSn-Mg-Znめっき浴（温度350℃）に導入した。めっき浴と鋼板表面を十分に反応させた後めっき浴より鋼板を引き出し、ガスワイピング法により付着量調整を行い急速冷却した。めっき後の鋼板は、0.7μmのFeSn<sub>2</sub>を主体とする合金層と付着量（Sn+Mg+Znの全付着量）32g/m<sup>2</sup>（片面あたり）のめっき層を有するものであった。この表面上にクロムとして15mg/m<sup>2</sup>の付着量のクロメート処理を行い製品板とした。

【0028】この鋼板の結晶組織を調べるため、1%塩酸で表面を軽く腐食したところ肉眼で認められる結晶組織が現れ、その長軸寸法の平均値は6mmであった。断

面研磨後、SnとMgとZnの分布状態をEPMA（電子プローブマイクロアナライザー）にて分析したところ、均一な分布状態が確認された。圧力容器中にて、100℃で一昼夜放置した強制劣化ガソリンに10vol%の水を添加し腐食液を作製した。この腐食液中にて、45℃×3週間の腐食試験を行ったところ、溶出した金属イオンはMgとZnが主体であり、合計で2100ppmの溶出が認められたが、良好な耐食性を示すものと判断された。

【0029】（比較例1）従来、ガソリタンク材料として使用されているターンシート（鉛-錫合金めっき鋼板）の付着量40g/m<sup>2</sup>の材料を、実施例と同様の腐食試験に供したところ、鉛が9700ppm、鉄が1200ppm溶出し、本発明鋼板より劣ることがわかった。

【0030】（比較例2）実施例2と同様の手順で、板厚0.8mmの焼鈍、調圧済みの鋼板に0.8g/m<sup>2</sup>の付着量の電気ニッケルめっきを施し、塩化亜鉛及び塩酸を含むめっき用フラックスを塗布した後、Mgを1.5%含む錫めっき浴（温度350℃）に導入した。めっき浴と鋼板表面を十分に反応させた後めっき浴より鋼板を引き出し、ガスワイピング法により付着量調整を行い緩冷却した。めっき後の鋼板は、0.5μmのFeSn<sub>2</sub>を主体とする合金層（17%のNi含有）と付着量（Sn+Mgの全付着量）33g/m<sup>2</sup>（片面あたり）のめっき層を有するものであった。この表面上にクロムとして12mg/m<sup>2</sup>の付着量のクロメート処理を行い製品板とした。

【0031】この鋼板の結晶組織を調べるため、1%塩酸で表面を軽く腐食したところ、緩冷却により大きな結晶が成長し、その長軸寸法の平均値は30.0mmであった。断面研磨後、SnとMgの分布状態をEPMA（電子プローブマイクロアナライザー）にて分析したところ、実施例2に比べ針状の巨大なMg<sub>2</sub>Sn結晶が多数観察され、SnとMgの偏析状態が確認された。実施例2と同様の腐食試験の結果、5200ppmのMg溶出が認められ、巨大なMg<sub>2</sub>Sn結晶による耐食性劣化が認められた。

【0032】  
 【発明の効果】本発明によって、耐食性、加工性、溶接性に優れ、劣化ガソリン等に対しても長期間耐える燃料タンク用の鉛フリー防錆鋼板が得られた。

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